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The Structure of Azoxy Compounds

THE STRUCTURE OF AZOXY COMPOUNDS

BY

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THESIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Milton Francis Tucker

ENTITLED. THE STRUCTURE OF AZOXY COMPOUNDS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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In

Chemical Engineering

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A C K N O W L E D G E M E N T

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INTRODUCTION

The structure of azoxy compounds has long been a subject of scientific research, and although much evidence is at present available which would tend to establish a correct formula for these compounds, yet it cannot be said that the actual structure is known.

The purpose of this work has been not to establish new evidence in favor of any structure but rather to reinvestigate a part of the extensive work carried on by Angeli¹ over a period of more than ten years. There are several points in his work which might be questioned, and it was hoped in this investigation to carry out the steps carefully and if possible to see whether there are any inaccuracies in the conclusions drawn.

Among the compounds prepared by Angeli, the mono-substituted azoxybenzenes which seemed of most interest are p-bromo-azoxybenzene, p-ethoxyazoxybenzene, and p-azoxybenzoic acid. Contradictory evidence was reported in an investigation² carried out at this University in 1919, and if the writer has aided in producing evidence in favor of either theory, he will consider the investigation as having contributed in part to the establishment of a correct formula for azoxy compounds.

A secondary problem in this thesis has been an attempted preparation of phloroglucinal by the condensation of acetone with malonic ester. The method for preparing this compound at present involves a number of steps and the yields are poor. If the compound could be prepared by the method attempted, a rather

cheap and efficient means of making phloroglucinol would be afforded. However, negative results were obtained and this problem was set aside.

H I S T O R Y

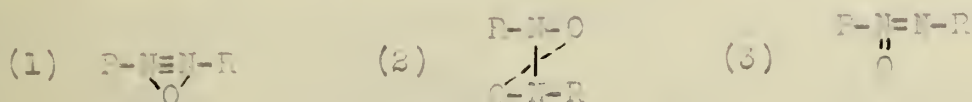
The first preparation of azoxy compounds dates back to 1845 when Zinnin³ prepared azoxybenzene by the action of alcoholic potash on nitrobenzene. Schraube⁴ in 1875 prepared p-azoxy-dimethylaniline by heating p-nitroso-dimethylaniline. In 1890 Gatterman and Fitschke⁵ reported the preparation of p-nitrophenetol-azoxyanisol by the action of sodium methylate on p-nitroanisol. The same compound was prepared by Rising⁶ in 1904. Nothing is said relative to isomeric compounds in either paper. The first mention of isomeric compounds was made in a paper by Janovsky and Reiman⁷ in 1889 in which isomeric forms of azoxy-toluenes were reported. Bamberger⁸ in 1900 reported isomers of o-hydroxyazoxybenzene. In 1909 Reissert⁹ prepared "isozoxybenzene" and "o-isozoxytoluene."

The greatest amount of work on various isomeric azoxy compounds was carried out by Angeli. He prepared a number of isomeric compounds, and as a result some authors are writing the formulas of azoxycompounds to comply with his theory.

Perhaps the most recent investigation on this problem was carried out by Meisenheimer¹⁰ in 1919. He prepared unsymmetrical azoxy compounds by the action of phenylhydroxylamine on nitro derivatives of benzene and reports the presence of isomers in all cases. His method of preparation might, however, lead to the formation of mixtures.

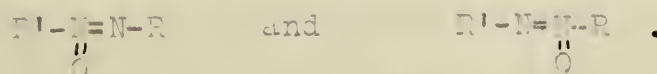
THEORETICAL PART

Among the various structures offered for azoxy compounds the one found in most text-books on organic chemistry is $R-\text{N}(\text{O})-\text{N}-R$. This was assigned by Zinnin, but inasmuch as it is not based on direct evidence, other alternative ones have been offered. Some of them are:-



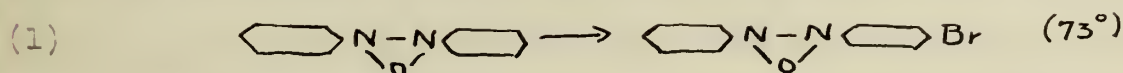
Brühl¹¹ suggested the first inasmuch as the refractive power of azoxybenzene is much greater than can be accounted for by Zinnin's formula. The second is reported by Hantzsch and Werner¹², the oxygen atoms being considered as half atoms. The third is given in Meyer & Jacobson's "Lehrbuch der Organische Chemie,"¹³ as one of the possible structures.

Angeli, in support of the latter structure, has shown that, when the compounds are unsymmetrical, isomers are formed. Thus we may have:-

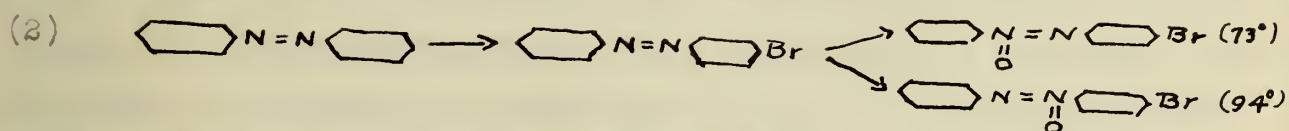


He prepared a number of such isomers, but a discussion of p-bromazoxybenzene will illustrate the theory.

Azoxybenzene was prepared by oxidizing azobenzene dissolved in acetic acid with 30% hydrogen peroxide. On brominating this compound pure crystals melting at 75° were obtained.

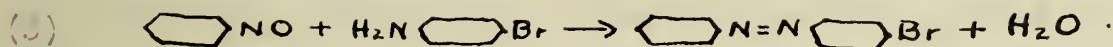


However, when azobenzene was first brominated and then oxidized, a mixture of two compounds was obtained. On separation with ligroin one melted at 73° and the other at 94° . Both were light yellow, of different crystalline form, and each yielded on reduction the same azo compound.



Since bromination of azobenzene, however, might lead to the formation of mixtures, it is obvious that erroneous results are possible.

In the present work it was hoped to prepare the p-bromoazobenzene as Angeli did and also as shown below, and after oxidation to compare results.



However, after several unsuccessful attempts to brominate azobenzene, the method was abandoned, and that given in (three) used, the p-bromoaniline having been prepared by saponifying p-bromoacetanilide. The azo compound was then oxidized in glacial acetic acid with 45% hydrogen peroxide prepared from 3% hydrogen peroxide according to Wolfenstein¹⁴. The red color of the solution changed to yellow after four weeks and on addition of water light yellow crystals were obtained.

The possibility of the catalytic effect of sunlight on the oxidation¹⁵ was investigated. Solutions of azobenzene in acetic acid containing hydrogen peroxide were made up in duplicate. One was placed in direct sunlight and the other in a dark

cabinet. After three weeks the colors of the solutions were compared but no visible difference was noted. The conclusion drawn from this is that sunlight does not exert a catalytic effect on this oxidation.

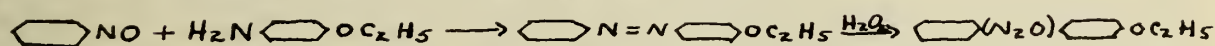
The p-bromoazoxybenzene was dissolved in ligroin then and crystallized fractionally. The material that first crystallized out always melted higher than the following portions. After a number of recrystallizations three sets of crystals were obtained which melted at 64° - 67° , 69° - 74° , and 89° - 91.5° respectively. An insufficient amount of material made it impossible to purify these further.

An interesting fact regarding the two isomers was brought out by Angeli in his endeavor to determine the structure of each. If $\text{C}_6\text{H}_4\text{N}=\text{N}\text{C}_6\text{H}_4\text{Br}$ is treated with bromine, $\text{BrC}_6\text{H}_4\text{N}=\text{N}\text{C}_6\text{H}_4\text{Br}$ is obtained. Brominating $\text{C}_6\text{H}_4\text{N}=\text{N}\text{C}_6\text{H}_4\text{NO}_2$ gives $\text{BrC}_6\text{H}_4\text{N}=\text{N}\text{C}_6\text{H}_4\text{NO}_2$ which is the same compound obtained by nitrating $\text{BrC}_6\text{H}_4\text{N}=\text{N}\text{C}_6\text{H}_4$. These facts indicate that the entering group goes in the para position to each $=\text{N}\text{C}_6\text{H}_4$ group, with perhaps in the case of bromine the formation first of a dibromo addition product ($=\text{N}(\text{C}_6\text{H}_4)\text{Br}_2$) and subsequent splitting off of HBr giving $=\text{N}(\text{C}_6\text{H}_4)\text{Br}$.

With this supposition granted the structure of the isomeric azoxy compounds may be determined. Thus, azoxybenzene gives with bromine p-bromoazoxybenzene melting at 73° . To this Angeli assigns the formula $\text{C}_6\text{H}_5\text{N}(\text{O})=\text{N}\text{C}_6\text{H}_4\text{Br}$. This compound does not yield a dibromo compound with bromine. The one melting at 94° must, therefore, have the structure $\text{C}_6\text{H}_5\text{N}(\text{O})=\text{N}(\text{C}_6\text{H}_4)\text{Br}$, and since it con-

tains a $\text{C}_6\text{H}_4\text{N}=\text{N}$ group in its molecule it forms as we should expect a dibromo compound.

The work with p-ethoxyazoxybenzene was very much the same as that with the bromo derivative. The compound was previously prepared through the following reactions:-



The substance was recrystallized in order to separate it into isomers. Petroleum ether was used as a solvent, and after some forty fractionations two sets of crystals were obtained which melted at $50^\circ\text{--}51.5^\circ$ and $71^\circ\text{--}74.5^\circ$ respectively. Both were light yellow. Again the compounds could not be sufficiently purified as not enough of the original mixture was available.

The possibility of incomplete oxidation resulting in a mixture of azo and azoxy compounds melting at a higher point than either is feasible, for in all the isomers prepared by Angeli the higher of any two has a melting point very close to the corresponding azo compound.

Accordingly, a portion of the lower melting p-ethoxyazoxybenzene was mixed in various percentages with p-ethoxyazobenzene and the melting point of each mixture taken. Nothing unusual was observed, for when the melting point was near 70° , the red color of the azo compound was very prominent.

At this time it was suggested that a means of separating two isomers might be afforded, if an alkaline solution of p-azoxybenzoic acid be acidified and the precipitate resulting from each addition of acid removed. The corresponding azo acid was prepared and then oxidized, but sufficient time was not available to complete this work.

From the evidence developed in this investigation it cannot definitely be said that two isomers are actually formed, although the presence of two sets of crystals melting at different points in both the bromo and ethoxy preparations cannot be denied.



EXPERIMENTAL PART

ATTEMPT TO PREPARE P-BROMOAZOXYBENZENE: An ice cold solution of 1 g. of azoxybenzene in the least amount of carbon tetrachloride was added through a dropping funnel into 0.9 g. of cold bromine. The container was placed in an ice bath for two minutes, then removed and allowed to assume room temperature. The excess solvent and bromine were then filtered from the reddish brown crystals of 4,4-dibromoazoxybenzene. These were washed with carbon tetrachloride, placed on a clay plate and exposed to the air. It was hoped that the compound would decompose partly to give p-bromazoxybenzene as stated by Angeli, but instead invariably the solid melted to a very dark oily substance on the slightest exposure.

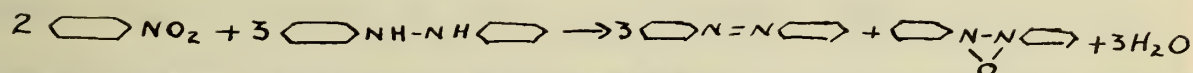
PREPARATION OF AZOBENZENE THROUGH HYDRAZO-BENZENE: Into a 5 liter flask fitted with a mechanical stirrer and reflux condenser 285 g. of zinc dust, 1 liter of alcohol, and 200 cc. of sodium hydroxide solution (3cc.= 1 gram) were placed. The flask was warmed in a water bath to about 50° and 150 g. of nitrobenzene added in small portions. Reduction took place almost immediately, and when all was added, the reaction mixture was filtered hot, cooled quickly, and the hydrazobenzene separated.

The crystals were placed in a flask with 500 cc. of alcohol and 5 cc. of sodium hydroxide solution (3cc.= 1 gram). A reflux condenser and glass tube reaching to the bottom of the flask were fitted in the stopper. The whole was heated on a water bath while a slow current of air was forced through the tube

into the solution during about 7 hours. The deep red colored solution was distilled until most of the alcohol was removed, and the azobenzene crystallized out by adding a little water. Yield 5.0 g. Melting point 67.5° - 68° .

ATTEMPT TO OXIDIZE HYDRAZOBENZENE WITH NITROBENZENE:

10 g. of hydrazobenzene were dissolved in about 100 cc. of alcohol and 3.3 g. of nitrobenzene added with 1 cc. of dilute sodium hydroxide solution. This was refluxed for two hours on a water bath until the solution became dark red. A little water was added and the precipitate filtered, washed with water, and recrystallized from alcohol. The melting point was 58° - 59° indicating that the compound was impure. Consultation of the literature proved that the reaction had been attempted and the equation presented as:-



The mixture was, therefore, distilled from iron filings and most of the azobenzene recovered.

ATTEMPT TO BROMINATE AZOBENZENE: 10 g. of azobenzene were dissolved in 50 cc. of acetic acid and warmed on a water bath at 50° - 60° . 9 g. of bromine were added slowly and after warming for 4 hours the solution was cooled, water was added, and the separated crystals filtered off. This was now placed in cold absolute alcohol and filtered. The filtrate was treated with water and the crystals filtered off and treated with 80% alcohol, in which the meta compound is more soluble than the para. The residue was separated and the melting point found to be 67° , indicating that the bromination had not taken place. Variations in the procedure did not meet with success.

PREPARATION OF NITROSOBENZENE: 15 g. of ammonium chloride were dissolved in 250 cc. of water contained in a 5 liter flask and 30 g. of nitrobenzene were added. 40 g. of zinc dust were added in small portions during a period of 15 minutes. The mixture was shaken vigorously after each addition of zinc and for 10 minutes after all was added. The temperature was maintained at 65° by cooling at intervals, and when the temperature ceased to rise, the mixture was filtered and the residue washed with 100 cc. of water at 60° . The filtrate was cooled in an ice bath and the phenylhydroxylamine salted out with sodium chloride. This was then filtered off and the phenylhydroxylamine immediately placed in a 5 liter flask. An ice cold solution of 180 g. of concentrated sulfuric acid in 900 cc. of water was added followed at once by the addition of an equally cooled solution of 34 g. of potassium dichromate in 1000 cc. of water. This mixture was shaken for several minutes and the precipitate filtered off immediately. It is important that this be carried out as quickly as possible, as the nitrosobenzene becomes very dark if allowed to remain in the mixture. The precipitate was washed with ice water and dissolved in the smallest amount of hot alcohol. A little boneblack was then added and the solution boiled for a few minutes. It was then filtered and cooled slowly. The nitrosobenzene crystallized out as very light brown crystals of sufficient purity to enable its use in the next synthesis. However, steam distillation of the product gave white crystals melting at $67.1^{\circ}-68^{\circ}$.

PREPARATION OF P-PHENOAZOBENZENE: 3 g. of nitrosobenzene were dissolved in the least amount of glacial acetic acid neces-

sally and a solution of 9.6 g. of p-bromaniline in glacial acetic acid added. The mixture was heated several minutes on a steam bath and then allowed to cool. This was then poured into about 300 cc. of water and the p-bromoazobenzene allowed to settle out. The crystals were filtered off, washed, free of acetic acid, and recrystallized from hot alcohol. Melting point 89.5° - 90° . Yield 7.5 g.

PREPARATION OF 45% HYDROGEN PEROXIDE: Into a two liter flask connected to a condenser and receiving flask under vacuum 2500 cc. of 3% hydrogen peroxide were added in portions and heated on a water bath maintained at a temperature of 50° . A capillary tube extending to the bottom of the flask fitted with a piece of rubber tubing and pinch-cock at the top made it possible to regulate the pressure, which was maintained at 40 mm. When the 2½ liters of hydrogen peroxide had been added and the resulting solution concentrated to about 150 cc., the solution was titrated with tenth normal potassium permanganate and it was found to be 45% hydrogen peroxide by weight.

OXIDATION OF P-BROMOAZOBENZENE: 5 g. of p-bromoazobenzene were dissolved in 500 cc. of glacial acetic acid and 10 cc. of 45% hydrogen peroxide added. The container was allowed to remain in the laboratory for two weeks after which the solution became orange in color. On precipitating out the compound by adding water a light orange precipitate was obtained melting at 79° - 83° . This was again taken up in glacial acetic acid and 7 cc. of hydrogen peroxide added. After a week a sample of the solution was poured into water and the crystals separated. They were orange colored and melted at 71° - 72° . The solution was

then placed in a water bath and kept at 50° at intervals during the time the writer was in the laboratory. After two weeks the orange color of the solution changed to a yellow and the crystals from this showed no trace of red. Melting point 66° - 69.5° .

Yield 7 g.

FRACTIONAL CRYSTALLIZATION OF P-BROMOAZOXYBENZENE: The crystals were placed in a small beaker and dissolved in the least amount of hot ligroin (B.P. 60° - 70°) necessary. The solution was allowed to cool slowly, and when a small portion of crystals separated out the liquor was decanted, the crystals separated, and the melting point taken. The remaining solution was allowed to cool further and another lot of crystals removed. This was repeated until the solution would yield no more crystals. It was then concentrated by distillation and the above process repeated. When most of the crystals had been removed, the filtrate was red, perhaps due to the presence of azo compound or to a secondary reaction with the air.

The fractions obtained were then recrystallized in the same manner as before, uniting two or more portions of crystals when their respective melting points were close. The ultimate results was a set of crystals melting at 89° - 91.5° and two portions melting at 69° - 74° and 64° - 67° respectively. Between these extremes a number of fractions were obtained melting throughout the range. A chart of the fractionation is given in the accompanying graph (Fig. I.).

FRACTIONAL CRYSTALLIZATION OF P-ETHOXYAZOXYBENZENE: The crystals were dissolved in petroleum ether (B.P. 50° - 55°) and placed in a distilling flask. One-fifth of the solvent was

removed by distillation, the solution cooled, and the resulting crystals separated. The filtrate was again distilled until another one-fifth portion was boiled off and again the crystals were separated. Thus five sets of crystals were obtained and these were again fractioned into various portions as indicated in Fig. II.. Ten sets of crystals finally remained, the melting points of the extremities being 50° - 51.5° and 71.5° - 74° .

MIXED MELTING POINT DATA OF SYSTEM: P-ETHOXYAZOXYBENZENE AND P-ETHOXYAZOBENZENE: 0.5 g. each of the two compounds were placed in small Erlenmeyer flasks and 25 cc. of alcohol added to each. By means of a pipette various portions from each were taken out and mixed on watch glasses. When the alcohol evaporated, an intimate mixture of crystals was obtained, and the melting point taken. The curve of this system is given on the following page. (Fig. III).

PREPARATION OF P-AZOPENZOIC ACID: 5 g. of nitrobenzene were dissolved in glacial acetic acid and a solution of 8.1 g. of p-aminobenzoic acid in glacial acetic acid added. The reaction mixture was warmed on a steam bath for about three minutes and then set aside for twenty minutes. It was then poured into the least amount of water necessary to precipitate the crystals. (Too much water must not be added as a colloidal suspension results). They were then filtered off and recrystallized from alcohol. This gave a brown product melting at 238° . Yield 4.5 grams.

OXIDATION OF P-AZOPENZOIC ACID: The details of this oxidation are the same as those given for p-bromoazobenzene. The product was light orange and melted at 240° - 241° .

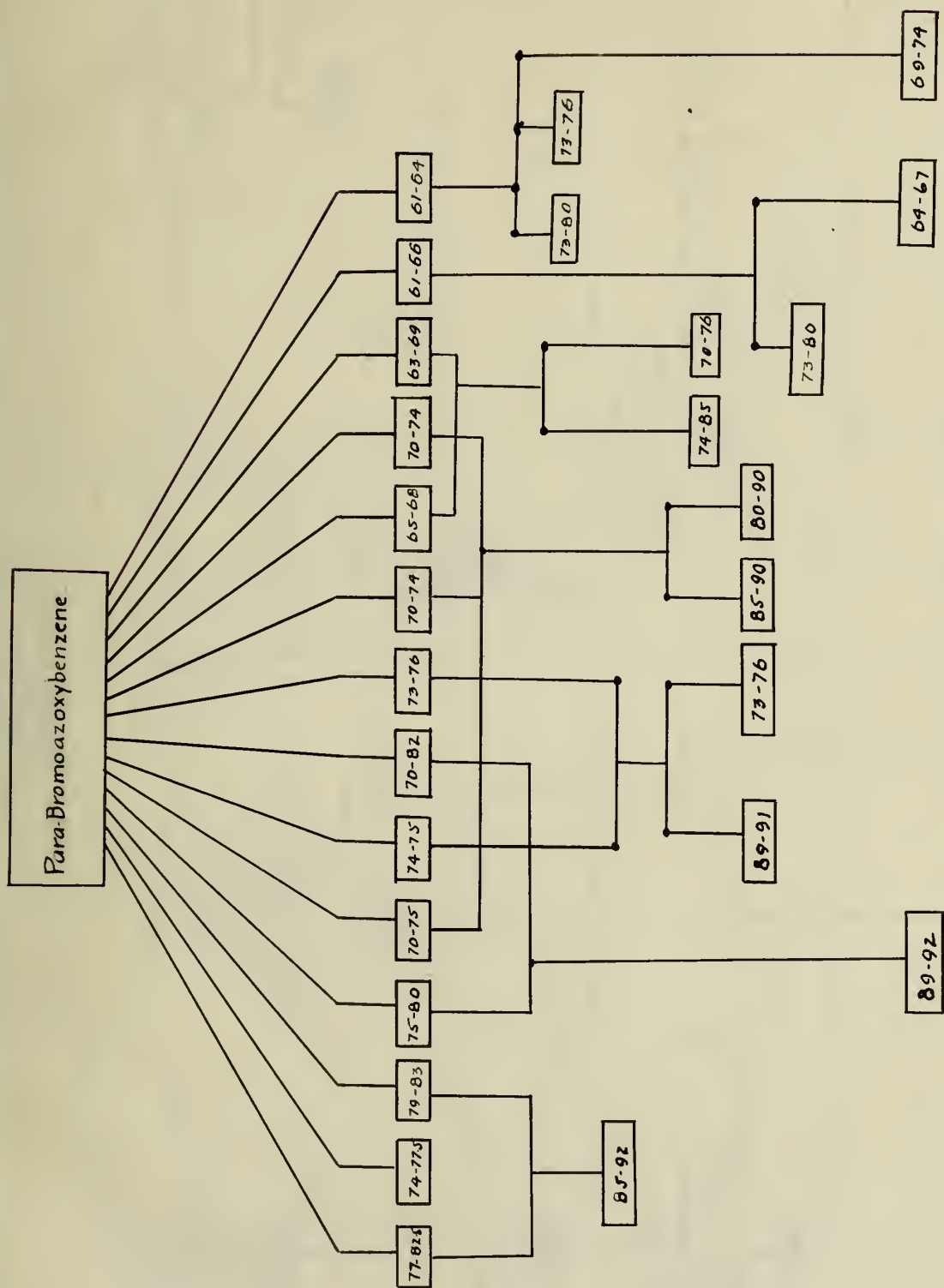


Fig. I



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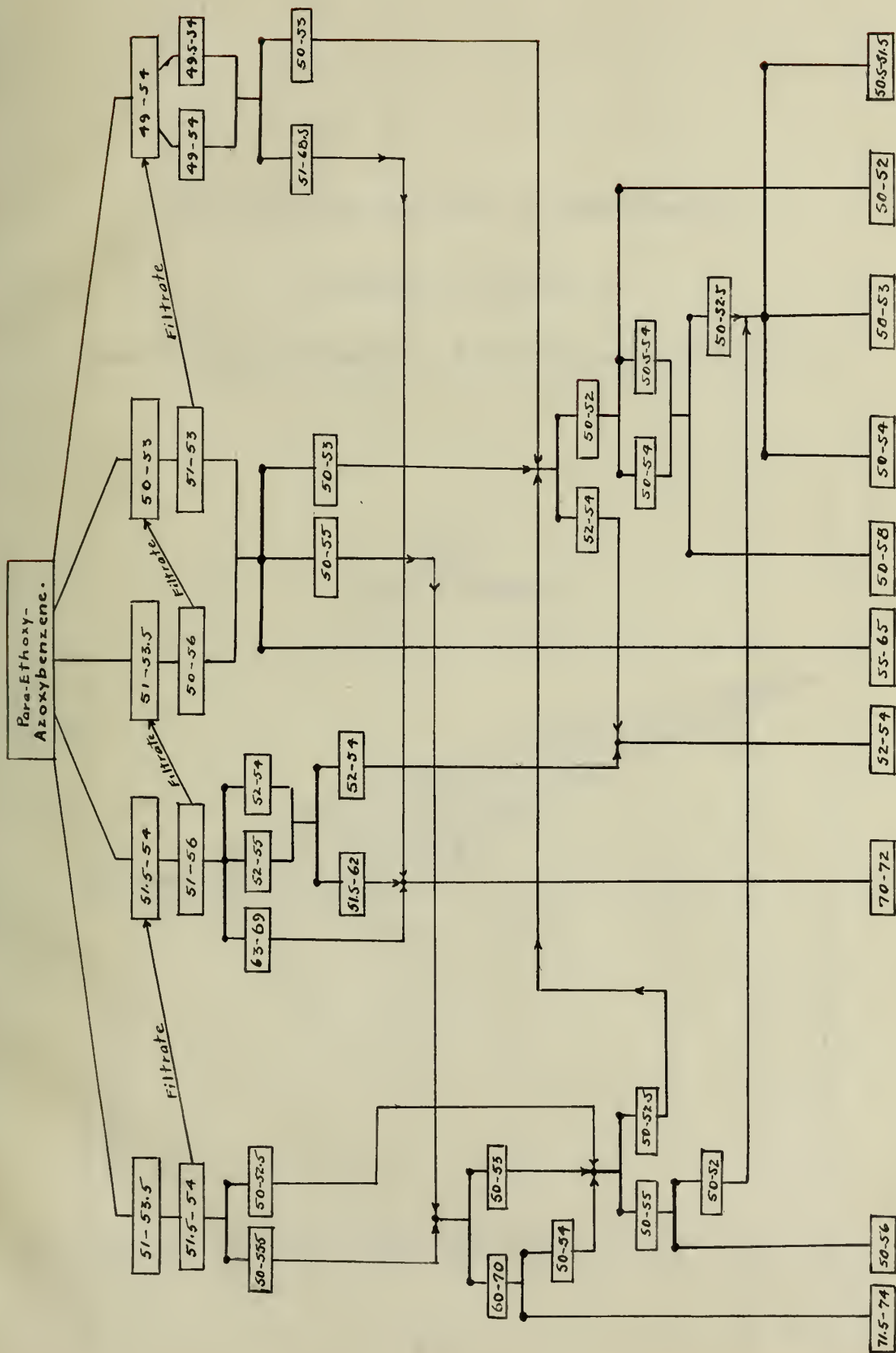


Fig. II

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Curve Showing the Melting Point Range
of Various Mixtures of
Para-Ethoxyazobenzene⁹³ & Para-Ethoxyazoxybenzene.

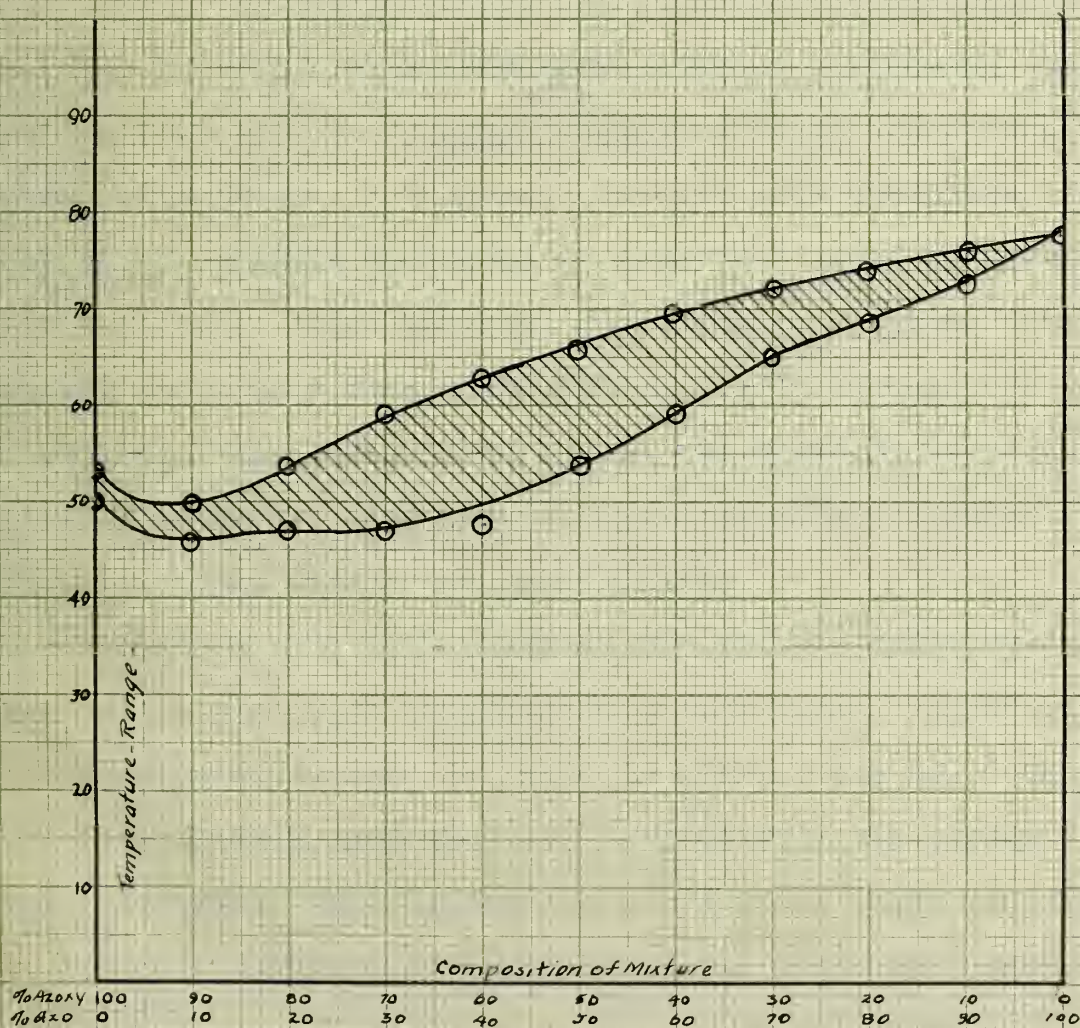
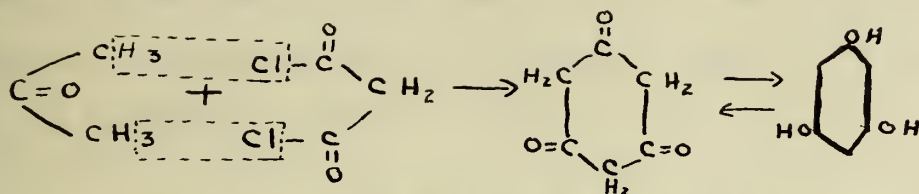


Fig. III

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PREPARATION OF PHLOROGLUCINOL: Phloroglucinol has been prepared by the action of acetone on malonyl chloride¹⁶ according to the following reaction:-



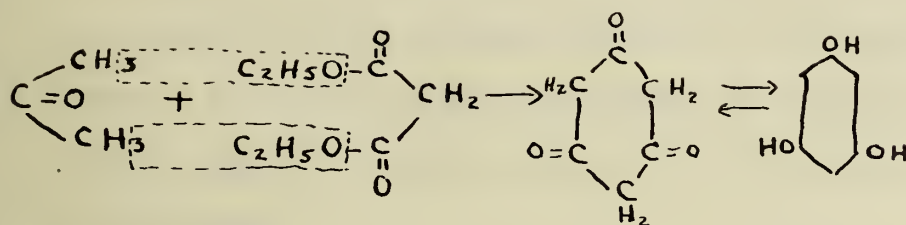
In the present work it was thought that a condensation with malonic ester would work equally well, with the added advantage that malonic ester is much more easily prepared than malonyl chloride. Accordingly, the following procedure was carried out.

50 g. of malonic ester and 36 g. of dry acetone were placed in a 500 cc. flask connected with a reflux condenser. An oil bath kept at 105° was placed around the flask and pieces of sodium dropped in. A vigorous reaction with evolution of heat took place. Sodium was added at intervals until no more went into solution. After 2½ hours the whole mass became thick, preventing the sodium from distributing itself through the mass. On cooling, this solidified and it was taken up in water and filtered. The filtrate was acidified in order to procure the phloroglucinol, but an oil precipitated.

Working with test portions the oil was extracted with ether which gave upon evaporation a dark brown "tarry" substance. An unsuccessful attempt was made to extract the oil from its alkaline solution, and thus separate it from the sodium salt of phloroglucinol. Salting out the oil did not prove satisfactory.

A new portion of the material was then made, keeping the temperature of the oil bath at 150°. The same characteristic points in the condensation were noted. The solid material was

first taken up in ether and after many extractions the residue was dissolved in water and acidified. This time only a very small amount of oil precipitated which was removed by filtering through glass wool. The clear filtrate was evaporated, but sodium chloride was the only residue found. The reaction hoped for is represented as:-



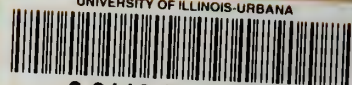
S U M M A R Y

- (1) Two substances of different melting points are formed in the oxidation of p-bromoazobenzene to p-bromoazoxybenzene.
- (2) Two substances of different melting points are formed in the oxidation of p-ethoxyazobenzene to p-ethoxyazoxybenzene.
- (3) Mixtures of azo and azoxy compounds of varying percentages did not show any resemblance to the substances referred to in (2) above.
- (4) Direct sunlight has no effect on the time required to oxidize azo compounds with hydrogen peroxide in glacial acetic acid.
- (5) Continued heating and sufficient time are controlling factors in obtaining complete oxidation of azo to the corresponding azoxy compounds.
- (6) Phloroglucinol could not be prepared by condensing acetone with malonic ester by means of metallic sodium.

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